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# Fabrication of a porous Pd film on nanoporous stainless steel using galvanic replacement as a novel electrocatalyst/electrode design for glycerol oxidation

Behzad Rezaei*, Elaheh Havakeshian, Ali A. Ensafi

*Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111 I.R. Iran*

A B S T R A C T

In this work, nanoporous stainless steel (NPSS) prepared by anodization process was used as an electrode material to support noble metal-based catalysts. To decorate NPSS with Pd, copper was deposited into the pores of NPSS using pulsed electrodeposition, and followed by the galvanic replacement reaction between deposited Cu and $PdCl_2$ solution. The surface morphology and composition of the prepared electrode were determined using scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive X-ray spectroscopy (EDS). SEM and AFM images showed that self-organized nanopores with an average size of about 77 nm were formed on the stainless steel surface and then were successfully filled with Cu. Galvanic replacement resulted in the formation of a porous film with a high electrochemically active surface area (EASA = 173.4 $cm^2$ $mg^{-1}$) and greatly reducing Pd loading (29 $\mu g\,cm^{-2}$). The EDS analysis revealed the presence of Cu and Pd in the prepared electrode (NPSS/Cu/Pd). Cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and chronoamperometry techniques were used to investigate the electrochemical behavior of the NPSS/Cu/Pd electrode in alkaline media. It was found that the porosity of NPSS and the presence of Cu improve the long-term stability of the Pd film on the surface. The electrode exhibited a remarkable catalytic activity for electrooxidation of glycerol due to the large EASA. The obtained mass activity and onset potential for glycerol oxidation were 0.82 mA $\mu g_{Pd}^{-1}$ and −0.35 V, respectively, which are acceptable as compared with those of palladium-carbon substrates. The results also indicated that the presence of Cu has a significant effect on the catalytic activity, the reaction kinetics and poisoning tolerance of the NPSS/Cu/Pd electrode. Accordingly, NPSS/Cu/Pd can be extended as a promising electrode for alcohol electrooxidation reactions in fuel cells and sensors.

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## 1. Introduction

Noble metal-based nanomaterials, due to their unique physiochemical, electrical and catalytic properties, have been reported as the most effective catalysts for a lot of electrochemical devices such as sensors and fuel cells [1–4]. However, their prohibitive cost and gradual loss of their performance under operating conditions restrict their wide practical applications. Therefore, many attempts have been made to the design and synthesis of advanced catalysts to reduce noble metal loading amounts and meantime enhance their catalytic activity, stability and utilization efficiency [3]. Moreover, it is well known that the properties of the electrode substrate (support) will influence the catalytic performance of

the heterogeneous electrocatalysts. Therefore, the development of novel support materials which facilitate electron transfer, increase long-term stability of the catalysts and allow fast mass transport of target analytes at the electrodes is highly desirable [5].

In the past decades, nanoporous materials, due to their high active surface area, large porosity and versatile porous structure, have attracted considerable interest in catalytic applications. Indeed, catalysts with a nanoporous structure provide more catalytic sites and facilitate the transport of the target analytes to the active sites in the nanopores [6]. On the other hand, since nanoporous materials have great ability to adsorb and interact with atoms, ions and molecules on their large interior surfaces and in the nanometer sized pore space, the catalytic properties and the long-term stability of the catalysts supported on a nanoporous substrate are better than those on the non-porous one [7,8].

Stainless steel, one of the most widely used alloys in industrial and biomedical applications, has novel characteristics such as low

cost, commercial availability, high corrosion resistance, mechanical strength and electrical conductivity. Moreover, it has been proved that the modification of stainless steel surface with nanostructures and catalysts such as oxide metals and noble metals improves its physiochemical and electrical properties and introduces catalytic properties [9–11]. Anodization is an inexpensive, simple and effective technique for the formation of highly ordered and size controlled nanopores over the macroscopic surface area. The formation of the self-organized nanoporous anodic layer onto stainless steel using anodization has been investigated in the literature [12–15]. Here, decorating NPSS with noble metal-based catalysts and considering their electrocatalytic behavior are of considerable interest.

The nanopores on nanoporous stainless steel can provide confined spaces for the growth and stabilization of metal nanostructures. Electrochemical deposition has been proved as a simple, inexpensive, controllable and efficient method to fill the nanopores with metals from the pore bottom towards the surface [16,17]. Nevertheless, the complete filling of pores with noble metals is not suitable for catalytic applications because a large amount of them is deposited at the bottom of the pores, where they are not accessible, which results in high catalyst loading without any improvement in catalytic utilization efficiency. Galvanic replacement, which is based on the spontaneous redox replacement of a less-noble metal with a nobler one, can provide a simple and effective method to make a wide variety of uniform porous bimetallic nanostructures with unique electronic properties and low noble metal loading [18,19]. However, since a metal oxide overlayer covers the surface of the NPSS [20], the direct spontaneous deposition of noble metals on the NPSS surface through the galvanic replacement process is impossible. Herein, the galvanic replacement of a less precious metal which has been electrodeposited into the nanopores with a noble metal can be useful.

In this work, nanopores formed on the anodized stainless steel substrate were filled with Cu metal (a less precious metal) using pulsed electrodeposition method. Then palladium (Pd) was deposited spontaneously on the Cu/NPSS electrode through the galvanic replacement process and characterized using SEM, AFM and EDX. Finally, the electrocatalytic activity and stability of Pd/Cu/NPSS electrode were investigated for the oxidation of glycerol in alkaline medium and compared with those of Pd/NPSS and Pd/Cu/SS electrodes.

## 2. Experimental

### 2.1. Reagents

Glycerol was obtained from Hopkin and Williams Ltd. Perchloric acid (70% $HClO_4$), boric acid, ethylene glycol, potassium hydroxide, $CuSO_4.3H_2O$ and $PdCl_2$ were purchased from Merck. Double-distilled water was used throughout the experiments.

### 2.2. Apparatus

Anodizing was performed using a homemade DC power supply. An Autolab PGSTAT 30 (Echo Chemie, The Netherlands) with a conventional three-electrode cell containing a platinum rod counter electrode, a saturated Ag/AgCl reference electrode and a modified stainless steel working electrode were used for Cu and Pd electrodeposition and all electrochemical measurements. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) images were taken using a field emission scanning electron microscope (FESEM, Hitachi S4160) operated at an accelerating voltage of 20.0 kV and an atomic force microscope (BRUKER, Germany), respectively. The catalyst chemical composition analysis was performed using an energy dispersive X-ray spectrometer (EDS) attached to the SEM (Seron technology AIS2300 C). To determine the amount of Pd loading, an inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7300DV; USA) was used to determine Pd dissolved from the electrode surface in hot aqua regia.

### 2.3. Electrode preparation

A 304 type stainless steel rod with a diameter of 3 mm was used as the substrate. It was embedded into Teflon to obtain an electrode with a geometric area of 0.07 cm². The stainless steel electrode was mechanically polished with emery paper (grade 500 and 1000), followed by 0.3 and 0.05 μm alumina slurry until a mirror finish was obtained. After each polishing step, the electrode was ultrasonically washed in ethanol and distilled water for 10 min.

Self-organized nanoporous anodic film was formed on the stainless steel (SS) surface via the anodization process, which has been explained in detail in the literature [12,20]. Briefly, SS (anode) was placed 1 cm away from a flat copper plate (cathode) in the ethylene glycol electrolyte containing 5 vol.% $HClO_4$, and then anodized at a constant voltage of 35 V for 15 min (time required to reach the steady state conditions). During the anodization process, the electrolyte was vigorously stirred and its temperature was maintained between 0 and 5 °C. The anodized electrode was then ultrasonically washed in ethanol and distilled water for 10 min and dried in a nitrogen stream.

Cu was electrodeposited into the nanopores of the NPSS electrode from a dearated solution of 10 g L⁻¹ $CuSO_4.3H_2O$ and 30 g L⁻¹ boric acid by applying pulse potential waveforms with different pulse durations (pulsed electrodeposition technique). In a modified condition, a cathodic pulse potential of -5.0 V for 4 ms, an anodic pulse potential of 0.1 V for 26 ms and a delay time of 900 ms were applied in each cycle, respectively. The cycle was continually repeated 9 times.

For spontaneous deposition of Pd, after Cu electrodeposition the electrode was immediately immersed into a 0.1 M $HClO_4$ solution containing 1 mM $PdCl_2$ for 30 min (the optimal time). Scheme 1 displays the overall procedure used to prepare the above electrode, which was named Pd/Cu/NPSS.

For comparison, Pd/Cu/SS electrode was prepared using the nonporous SS under the same conditions and Pd/NPSS electrode was prepared by electrodeposition of Pd into the pores of NPSS electrode.

### 2.4. Electrochemical measurements

All electrochemical measurements were performed in 1.0 M KOH aqueous solution in the absence or presence of 5 wt% glycerol at room temperature. Prior to each experiment, nitrogen gas was bubbled through the electrolyte for 15 min to remove the oxygen from the electrolyte. In cyclic voltammetry experiments, the potential was scanned from −1.0 to 0.2 V at a scan rate of 50 mV
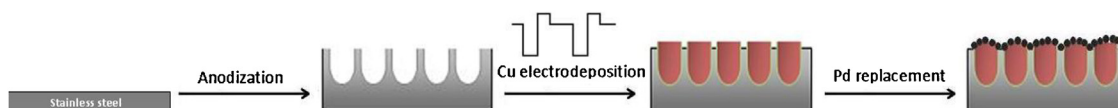


**Scheme 1.** Schematic illustration of the procedure for preparing NPSS/Cu/Pd electrode.